Coulomb interaction and ferroelectric instability of $BaTiO_3$

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Abstract

Using first-principles calculations, the phonon frequencies at the Γ point and the dielectric tensor are determined and analysed for the cubic and rhombohedral phases of $BaTiO_3$. The dipole-dipole interaction is then separated à la Cochran from the remaining short-range forces, in order to investigate their respective influence on lattice dynamics. This analysis highlights the delicate balance of forces leading to an unstable phonon in the cubic phase and demonstrates its extreme sensitivity to effective charge changes. Within our decomposition, the stabilization of the unstable mode in the rhombohedral phase or under isotropic pressure has a different origin.

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Barium Titanate ($BaTiO_3$) is a typical ferroelectric material that undergoes three temperature phase transitions, from a paraelectric cubic phase, stable at high temperature, to ferroelectric phases of tetragonal, orthorhombic and rhombohedral symmetry. There have been considerable efforts to identify the origin of the transitions in this particular ABO_3 compound [1]. Among them, let us point out the seminal theory of Cochran [2]. In the framework of a shell model, he relates the ferroelectric transition to the softening of a transverse optic phonon at Γ. Within his model, the interatomic forces are decomposed into short-range forces and long-range Coulomb (dipole-dipole) interaction. The latter is evaluated by means of a Lorentz effective electric field, assuming a local spherical symmetry at each atomic site. Interestingly, the decomposition isolates the contribution of each kind of forces on the frequency of the transverse modes and identifies the structural instability with the cancellation of the two contributions. Although meaningful, Cochran's model is only qualitative. The numerical investigation is subject to many approximations. Moreover, it was shown by Slater [3] that the Lorentz field is far from spherical.

In subsequent studies, it has been usually accepted that ferroelectricity in perovskites results from a delicate balance between short-range repulsions which favor the cubic phase and long-range electrostatic forces which favor the ferroelectric state. Although some calculations [4] illustrate this picture, they do not rely on a well defined separation of the interactions.

In contrast, a separation of the interatomic forces was proposed recently by Gonze *et al.* [5]. Without postulating any atomic site symmetry, they introduce an analytic form for the dipole-dipole interaction at the microscopic level from Born effective charges and dielectric tensor. This formulation, evaluated thanks to first-principles data, generalizes Slater's calculation of the Lorentz field [3] and can be used to refine Cochran's results [2].

In our letter, we consider the cubic and rhombohedral phases as well as a compressed cubic structure. We first report dielectric tensor values, then compute the dynamical matrices and phonon frequencies at the Γ point and compare them with experiment. Separating a dipole-dipole interaction from the short-range remaining part of the dynamical matrix

following Gonze *et al.* [5], we quantify the balance of forces generating the unstable cubic phonon mode and investigate its sensitivity to effective charge changes. Within this decomposition, the hardening of the unstable phonon in the rhombohedral phase or under isotropic pressure has a different origin.

Computational details are the same as in Ref. [6–8]: Calculations are performed within the Density Functional Theory (DFT) and the Local Density Approximation (LDA) using a conjugate-gradient plane-wave pseudopotential method. Responses to electric field and phonon-type perturbations are obtained within a variational approach to Density Functional Perturbation Theory.

We consider cubic structures at the experimental and theoretically optimized volumes with lattice parameters a_o = 4.00 and 3.94 Å, as well as a compressed cubic cell with a_o=3.67 Å. For the rhombohedral phase, we worked at the experimental unit cell parameters, with relaxed atomic positions. Accurate values for the Born effective charges $Z^*_{\kappa,\alpha\beta}$ were already reported elsewhere [8].

The computed dielectric tensor ϵ_∞ is presented in Table I in comparison to its experimental estimate in the cubic phase [9]. No previous values were reported for the rhombohedral phase. It is well known that the DFT-LDA usually overestimates the experimental ϵ_∞. For the cubic geometry, the discrepancy is of the order of 25%. This error can be corrected in first approximation by the *scissor operator* technique [10]. For all cases, we have used a scissor shift of $1.36\,eV$ that adjusts the bandgap at the Γ point in the experimental cubic structure to the value of $3.2\,eV$ [1]. For the cubic phase, the scissor corrected ϵ_∞ (5.61) overestimates the experimental value (5.40) by less than 5%. For the rhombohedral structure, the values are globally smaller, especially along the ferroelectric axis. This goes hand-in-hand with the reduction also observed in this direction for Z^*_κ [8].

There are 12 optical phonons in $BaTiO_3$. In the cubic phase, we have three triply degenerate modes of F_{1u} symmetry and a triply degenerate mode of F_{2u} symmetry. Only the F_{1u} modes are infrared active, with LO-TO splitting, while the F_{2u} modes are *silent* modes that cannot be identified experimentally. Our values (Table II) at the optimized

volume are in close agreement with the experiment [11] as the theoretical results of Zhong *et al.* [12]. In particular, we reproduce the instability of the TO1 mode corresponding to the vibration of Ti and Ba against the O atoms. The phonon frequencies appear very sensitive to the small volume change from the experimental to the theoretical cubic phase, contrary to Z^*_κ [8] or ϵ_∞. This is particularly true for the soft TO1 mode, whose instability even disappears in our compressed cubic phase.

Due to the long-range Coulomb interaction, the eigendisplacements of the TO modes (η^{TO}) do not necessarily correspond to those of the LO modes (η^{LO}). The overlap matrix $\langle \eta^{TO} | M | \eta^{LO} \rangle$ reported in Table III establishes however that the mixing of modes is very weak in the cubic phase (M is such that $M = M_\kappa \delta_{\kappa\kappa'}$ with M_κ is the mass of atom κ). In agreement with this observation, assuming that η^{LO} and η^{TO} are identical, the fictitious LO frequencies predicted on the basis of the oscillator strengths (Eq. 10 of Ref. [6]) are respectively of 701, 214 and 508 cm^{-1}, in close agreement with the theoretical LO frequencies. Note the giant splitting of the TO1 mode already mentioned by Zhong *et al.* [12]. It arises from the large effective charges on Ti ($Z^*_{Ti} = +7.28$) and O ($Z^*_{O_\parallel} = -5.73$, for a displacement along the Ti-O bond) generating a mode effective charge $Z^*_{TO1} = \left\| \frac{\sum_{\kappa,\beta} Z^*_{\kappa,\alpha\beta} \eta^{TO1}_{\kappa,\beta}}{\langle \eta^{TO1} | \eta^{TO1} \rangle} \right\| = 9.02$.

In the rhombohedral phase (Table II), each triply degenerate F_{1u} (resp. F_{2u}) mode from the cubic phase gives rise to a mode of A_1 (resp. A_2) symmetry with eigendisplacements along the ferroelectric direction, and a doubly degenerate mode of E symmetry. E and A_1 modes are infrared and Raman active. The only relevant comparative result we found is experimental [13] and localizes the phonon frequencies in three regions (100-300 cm^{-1}, 480-580 cm^{-1}, and 680-750 cm^{-1}) in qualitative agreement with our values.

All the modes are stable in the rhombohedral structure. Due to the small distortions, the eigenvectors remain very similar to those of the cubic phase. Table III compares A_1 to corresponding F_{1u} eigenvectors. Similar values are obtained for the E modes. They point out that $A_1(TO2)$ and $E(TO2)$ originate from the hardening of the soft mode. Even if both of these modes continue to couple strongly with the electric field, the smaller Z^*_κ make their mode effective charge smaller: 7.00 and 8.41 respectively. We predict a static dielectric

constant equal to 33.09 along the ferroelectric direction and to 68.89 perpendicularly to it.

The phonon frequencies ω and the associated eigendisplacements η are deduced from the dynamical matrix A through the following equation: $\sum_{\kappa'\beta} A_{\alpha\beta}(\kappa\,\kappa')\,\eta_{\kappa',\beta} = M_\kappa\,\omega^2\,\eta_{\kappa,\alpha}$. The α and β indices denote the space direction while κ and κ' label the atom within the unit cell. The ansatz proposed by Gonze *et al.* [5] can now be used to parametrize the dipole-dipole contribution to the interatomic force constant from the knowledge of Z^*_κ and ϵ_∞, in the general case where these tensors are anisotropic [14]:

$$\Phi^{DD}_{\alpha\beta}(0\kappa, j\kappa') = \sum_{\alpha'\beta'} Z^*_{\kappa,\alpha\alpha'}\,Z^*_{\kappa',\beta\beta'}\,(det\,\epsilon_\infty)^{-\frac{1}{2}}\left(\frac{(\epsilon^{-1}_\infty)_{\alpha'\beta'}}{D^3} - 3\frac{\Delta_{\alpha'}\Delta_{\beta'}}{D^5}\right)$$

where $\Delta_\alpha = \sum_\beta(\epsilon^{-1}_\infty)_{\alpha\beta}\,d_\beta$, $\vec{d} = \vec{R}_j + \vec{\tau}_{\kappa'} - \vec{\tau}_\kappa$ is the vector relating nuclei , and $D = \sqrt{\vec{\Delta}.\vec{d}}$. The contribution of this dipole-dipole term to the dynamical matrix is evaluated using Ewald summation technique [5]. By this way, dipole-dipole (DD) and remaining short-range (SR) [15] parts of the dynamical matrix A can be isolated from each other *à la Cochran* ($A = A_{DD} + A_{SR}$) and their partial contribution to ω^2 can be evaluated as follows:

$$\underbrace{\langle\eta|A|\eta\rangle}_{\omega^2} = \underbrace{\langle\eta|A_{DD}|\eta\rangle}_{\omega^2_{DD}} + \underbrace{\langle\eta|A_{SR}|\eta\rangle}_{\omega^2_{SR}}.$$

A_{DD} and A_{SR} can then be modified independently in order to investigate their own influence on the instable mode.

In Table IV we report the values of ω^2_{DD} and ω^2_{SR} for the TO modes of the cubic phase at the optimized volume. We observe that the instability of the $F_{1u}(TO1)$ mode originates from the compensation of two very large numbers, the DD interaction greatly destabilizing the crystal. Interestingly, this close compensation exists for the unstable mode *only*.

In the cubic phase, the large values of Z^*_{Ti} and $Z^*_{O_\parallel}$ (responsible of the strong Coulomb interaction) are mainly produced by a dynamic transfer of charge along the Ti-O bond [8]. Postulating A_{SR} to be fixed, we can fictitiously reduce this transfer of charge by decreasing simultaneously Z^*_{Ti} and $Z^*_{O_\parallel}$, and monitor the $F_{1u}(TO1)$ mode frequency changes. Figure 1 shows that $\omega^2(TO1)$ evolves quasi linearly with the transfer of charge. A change corresponding to a reduction of the order of 1% of Z^*_{Ti} is enough to *suppress* the instability. Of course

this situation is artificial: In a real material any modification of Z^*_κ would go hand-in-hand with a change of the SR forces. This result however highlights the very delicate compensation existing between DD and SR interactions. Interestingly, ω^2_{SR} is also modified, due to the change of the eigenvector η induced by the modification of A_{DD}. This change is not crucial and a similar evolution of ω^2 is observed if we keep the eigenvector of the original optimized structure. Note that all these conclusions are independent of the use of the scissor correction for ϵ_∞. From now, we report results without scissor correction.

In the rhombohedral structure, there is no unstable mode although the eigenvectors remain close to those of the cubic phase (see Table III). It was found [8] that Z^*_κ are smaller in this ferroelectric phase, suggesting a smaller DD interaction, but this could be partly compensated by a reduction of ϵ_∞. For the $A_1(TO2)$ mode coming from the soft mode, ω^2_{DD} (-286267 cm^{-2}) add to a slightly larger SR counterpart (356373 cm^{-2}). The values differ widely from those of the cubic phase: The SR forces give less stabilization but this is compensated by a larger reduction of the DD contribution.

If we now fictively modify A_{DD} and replace Z^*_κ and ϵ_∞ of the ferroelectric structure by their value in the cubic phase, we modify the frequency of the $A_1(TO2)$ mode from 265 to $266i$ cm^{-1}: We obtain an instability even *larger* than in the cubic phase. From this point of view, the reduction of Z^*_κ in the rhombohedral phase appears as a crucial element to the stabilization of the $A_1(TO2)$ mode. Introducing Z^*_κ and ϵ_∞ of the cubic phase, ω^2_{DD} and ω^2_{SR} are also strongly modified and becomes respectively -871017 and 800371 cm^{-2}. The dramatic change of ω^2_{SR} results from a change of eigenvector pointing out the anisotropy of the SR forces (the overlap between the new and original eigenvector is equal to 0.86). If we had kept the eigenvector unchanged, we would still have observed an instability ($74i$ cm^{-1}) for the $A_1(TO2)$ mode although much smaller. This means that the inclusion of the effective charges of the cubic phase is already sufficient to destabilize the crystal but at the same time produces a change of eigenvector enlarging the instability.

No more instability is present in the compressed cubic phase, although the global values of Z^*_κ do not differ significantly from those at the optimized volume [8]. Moreover, the

reduction of volume even increases the destabilizing effect of the DD interaction by 20%. However, strong modifications of the SR forces produce a mixing of modes so that no one can be identified with the unstable mode observed at the optimized volume. If we replace A_{SR} by its value at the optimized volume we recover a very large instability ($437i$ cm^{-1}). The disappearance of the unstable mode under pressure seems therefore essentially connected to a modification of the SR forces in contrast to its stabilization in the rhombohedral phase related to the reduction of Z^*_κ.

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[14] In this formula, the macroscopic ϵ_∞ is used to parametrize dipole-dipole interactions down to nearest neighbors. No correction for the q-dependence of ϵ_∞ and Z^*_κ is included. This procedure is the natural generalization of Luttinger and Tisza calculations [Phys. Rev. 70, 954 (1946)], basis of Slater evaluation of the Lorentz field [3].

[15] The SR part also contains higher Coulomb terms like dipole-octupole and octupole-octupole interactions.

FIGURES

FIG. 1. Evolution of the $F_{1u}(TO1)$ mode frequency squared with respect to the dynamic transfer of charge along the Ti-O bond (quantified here by the evolution of Z^*_{Ti}, see text). Results are obtained with ($\circ$) or without ($-\bullet-$) scissor shift for ϵ_∞. SR and DD contributions to ω^2 (see text) are shown in the inset.

TABLES

TABLE I. Dielectric tensor of $BaTiO_3$ obtained within the local density approximation (LDA) or with an additional scissor correction (SCI). For the rhombohedral phase, the z axis points in the ferroelectric direction.

	Cubic phase ($\epsilon_\infty^{xx} = \epsilon_\infty^{yy} = \epsilon_\infty^{zz}$)			Rhombohedral phase	
	$a_o = 3.67$ Å	$a_o = 3.94$ Å	$a_o = 4.00$ Å	$\epsilon_\infty^{xx} = \epsilon_\infty^{yy}$	ϵ_∞^{zz}
LDA	6.60	6.66	6.73	6.16	5.69
SCI	5.71	5.60	5.61	5.26	4.91

TABLE II. Phonon frequencies (cm^{-1}) at the Γ point for cubic and rhombohedral $BaTiO_3$.

	Cubic phase				Rhombohedral phase			
Mode	a_o=3.67Å	Exp. [11]	a_o=3.94Å	a_o=4.00Å	Mode		Mode	
$F_{1u}(TO1)$	214	soft	$113i$	$219i$	$A_1(TO1)$	168	$E(TO1)$	161
$F_{1u}(LO1)$	250	180	180	159	$A_1(LO1)$	180	$E(LO1)$	173
$F_{1u}(TO2)$	296	182	184	166	$A_1(TO2)$	265	$E(TO2)$	205
$F_{1u}(LO2)$	513	465	460	447	$A_1(LO2)$	462	$E(LO2)$	438
$F_{1u}(TO3)$	737	482	481	453	$A_1(TO3)$	505	$E(TO3)$	461
$F_{1u}(LO3)$	1004	710	744	696	$A_1(LO3)$	702	$E(LO3)$	725
F_{2u}	308	306	288	281	A_2	274	E	293

TABLE III. Overlap matrix elements between the eigenvectors of the $F_{1u}(TO)$ modes of the optimized cubic phase and those respectively of the associated $F_{1u}(LO)$ mode and of the $A_1(TO)$ mode of the rhombohedral phase.

	$F_{1u}(LO1)$	$F_{1u}(LO2)$	$F_{1u}(LO3)$	$A_1(TO1)$	$A_1(TO2)$	$A_1(TO3)$
$F_{1u}(TO1)$	0.17	-0.36	0.92	0.13	-0.97	-0.19
$F_{1u}(TO2)$	-0.99	-0.07	-0.16	-0.99	-0.13	-0.01
$F_{1u}(TO3)$	0.01	-0.93	0.37	-0.02	0.18	-0.98

TABLE IV. DD and SR contributions (see text) to the TO mode frequency squared (cm^{-2}) for the cubic phase at the optimized volume. Values in brackets where obtained with the scissor-corrected value of ϵ_∞.

	$F_{1u}(TO1)$	$F_{1u}(TO2)$	$F_{1u}(TO3)$	F_{2u}
ω^2_{DD}	-625897 (-745610)	7232 (8615)	-130549 (-155518)	109745 (130736)
ω^2_{SR}	613107 (732820)	26538 (25155)	361998 (386967)	-26951 (-47942)
ω^2	-12790	33770	231449	82794

Ghosez et al. Fig. 1